International Standard ISO 6332

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Water analysis — Determination of iron — 1,10-phenanthroline photometric method

Analyse de l'eau — Dosage du fer — Méthode spectrométrique à la phénanthroline-1,10

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Foreword

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It has been approved by the member bodies of the following countries :

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Netherlands
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Water analysis — Determination of iron — 1,10-phenanthroline photometric method

1 Scope and field of application

This International Standard specifies a 1,10-phenanthroline photometric method for the determination of iron in water and waste water. Procedures are described for the determination of total iron, total acid soluble iron, total dissolved iron and, if required, acid soluble and dissolved iron(II) and iron(III).

The method is applicable to the determination of iron concentrations between 0,01 and 5 mg/l. Iron concentrations above 5 mg/l may be determined after suitable dilution of the sample.

2 Reference

ISO 5667/1, *Water quality — Sampling — Part 1 : Guidance on the design of sampling programmes.*

3 Principle[1)]

Addition of 1,10-phenanthroline solution to a test portion and photometric measurement of the orange-red complex at a wavelength of about 510 nm.

If determining total iron, total acid soluble iron and total dissolved iron, hydroxylammonium chloride is added to reduce iron(III) to iron(II). If undissolved iron, iron oxides or iron complexes are present, pretreatment is necessary to bring such compounds into solution.

The iron(II)-1,10-phenanthroline complex is stable in the pH range from 2,5 to 9 and the intensity of the colour is proportional to the amount of iron(II) present. The relationship between concentration and absorbance is linear up to a concentration of 5,0 mg of iron per litre. Maximum absorbance occurs at about 510 nm [molar absorption coefficient 11×10^3 l/(mol·cm)].

4 Reagents

Use only reagents of recognized analytical grade.

The water used shall have as low an iron concentration as possible; a measurable iron concentration in the reagents is permissible provided that the lowest concentration to be determined is at least three times the standard deviation of the predetermined results of blank tests. Deionized water or water distilled from an all-glass apparatus has been found to be suitable.

4.1 Acetate buffer.

Dissolve 40 g of ammonium acetate (CH_3COONH_4) and 50 ml of glacial acetic acid (CH_3COOH) (ϱ = 1,06 g/ml) in water and dilute to 100 ml with water.

4.2 Di-isopropyl ether [$(CH_3)_2CH-O-CH(CH_3)_2$].

(ϱ = 0,72 g/ml), alcohol free, boiling point between 67 and 69 °C.

4.3 Hydrochloric acid solution, ϱ = 1,125 g/ml, $c(HCl) \approx 7{,}7$ mol/l.

1) For possible sources of interference and methods for their removal, see 7.2.1.2 and clause 10.

4.4 Hydroxylammonium chloride, 100g/l solution.

Dissolve 10 g of hydroxylammonium chloride ($NH_2OH{\cdot}HCl$) in water and dilute to 100 ml.

This solution is stable for at least 1 week.

4.5 Nitric acid, concentrated, ϱ = 1,40 g/ml.

4.6 1,10-phenanthroline solution.

Dissolve 0,5 g of 1,10-phenanthrolinium chloride (monohydrate) ($C_{12}H_9ClN_2{\cdot}H_2O$) in water and dilute to 100 ml.

Alternatively, dissolve 0,42 g 1,10-phenanthroline monohydrate ($C_{12}H_8N_2{\cdot}H_2O$) in 100 ml of water containing 2 drops of hydrochloric acid (3.3).

This solution is stable for 1 week if stored in the dark.

4.7 Potassium peroxodisulphate, 40 g/l solution.

Dissolve 4 g of potassium peroxodisulphate ($K_2S_2O_8$) in water and dilute to 100 ml.

This solution is stable for several weeks if stored at room temperature in a dark glass bottle.

4.8 Iron, standard solution corresponding to 0,10 g of iron per litre.

Weigh 50,0 mg of iron wire (purity 99,99 %) into a 500 ml volumetric flask. Add 20 ml of water, 5 ml of the hydrochloric acid solution (4.3), and warm gently to dissolve. Cool, and make up to the mark with water.

1 ml of this standard solution contains 0,10 mg of iron.

This solution is stable for at least 1 month if stored in a resistant glass or plastics bottle.

Commercial iron standard solutions may be used.

4.9 Sulphuric acid, ϱ = 1,84 g/ml.

4.10 Sulphuric acid solution, $c(1/2\ H_2SO_4) \approx 4,5$ mol/l.

Add slowly and with vigorous stirring 1 volume of concentrated sulphuric acid (4.9) to 3 volumes of water while cooling.

5 Apparatus

All glassware, including sample containers, shall be washed with hydrochloric acid and rinsed with water before use.

Usual laboratory equipment, and

5.1 Spectrophotometer, prism or grating type, suitable for making measurements at 510 nm; or **photoelectric absorptiometer,** fitted with a narrow band pass optical filter having maximum transmission in the region of 510 nm.

5.2 Photometric cells, of optical path length at least 10 mm and appropriate to the expected absorbance of the test solution.

NOTE — Cells of longer optical path length are preferable for determining iron concentrations less than 1,0 mg/l.

5.3 Membrane filter, average pore size 0,45 µm.

6 Sampling and preparation of test samples

WARNING — Appropriate safety precautions shall be taken when acidifying samples due to the possibility of release of toxic gases.

6.1 Sample

Take the sample in accordance with ISO 5667/1 and any specific recommendations for the type of water under examination. Appropriate containers such as polyethylene shall be used.

6.2 Total iron

Acidify the sample immediately after collection to pH 1. In general, 1 ml of concentrated sulphuric acid (4.9) is sufficient for 100 ml of sample. If necessary, adjust the pH by addition of dilute sulphuric acid (4.10) and take into account any dilution in the final calculations.

6.3 Total acid soluble iron and acid soluble iron(II)

Filter the acidified sample (6.2) through the membrane filter (5.3).

If it is intended to determine iron(II), this filtration should be carried out under an inert atmosphere, for example nitrogen or carbon dioxide, in order to exclude as much air as possible and thus to prevent oxidation of the iron(II).

Fill a glass sample bottle with the filtrate and continue until at least five times the volume has overflowed. Immediately close the bottle with a tightly fitting glass stopper.

6.4 Total dissolved iron

To separate dissolved iron from undissolved iron, filter the sample (6.1) immediately after collection through a membrane filter (5.3) and then acidify to pH 1 (see 6.2).

7 Procedure

7.1 Test portion

Take, as the test portion, 50,0 ml of the acidified test sample (clause 6).

7.2 Preparation of test solution

7.2.1 Total iron

If undissolved iron, iron oxides or iron complexes are present transfer the test portion (7.1) to a 100 ml boiling flask and carry out the following pretreatment.

7.2.1.1 Oxidation

Add 5 ml of potassium peroxodisulphate solution (4.7) and gently boil for about 40 min ensuring that the volume does not fall below about 20 ml. Then cool and transfer it to a one-mark volumetric flask of capacity 50 ml and make up to the mark with water.

NOTE — Alternatively, the mixture may be autoclaved in a 100 ml closed bottle for 30 min, then cooled and diluted to 100 ml. This dilution should be taken into account in calculating the result by multiplying by a factor of 2.

If the solution is turbid after oxidation and before dilution, filter it immediately through the membrane filter (5.3) into the volumetric flask. Rinse the filter with a small amount of water adding the washings to the filtrate and make up to the mark with water.

7.2.1.2 Removal of interferences

If removal of interferences is necessary (see clause 10) proceed as follows :

Transfer exactly 10 ml of the oxidized solution (7.2.1.1) to a 100 ml separating funnel and add 15 ml of hydrochloric acid solution (4.3). Cool and extract three times with 25, 10 and 10 ml portions respectively of di-isopropyl ether (4.2). Combine the ether phases in a second separating funnel and extract twice with 25 and 10 ml portions respectively of water. Combine the aqueous extracts and heat cautiously to remove residual ether. Cool, add 0,5 ml of sulphuric acid (4.10) and dilute to 50 ml with water.

7.2.1.3 Reduction to iron(II)

Transfer the whole of the solution from 7.2.1.1 or 7.2.1.2 to a 100 ml flask and add 1 ml of hydroxylammonium chloride solution (4.4) and mix thoroughly. Then add 2 ml of acetate buffer (4.1) to bring the pH to between 3,5 and 5,5, preferably 4,5.

NOTE — The reduction of iron(III) to iron(II) proceeds most effectively at pH 1. The buffer solution should therefore be added last.

7.2.2 Total acid soluble iron and total dissolved iron

Treat the test sample from either 6.2 or 6.3 according to the procedure described in 7.2.1. If the sample is known to contain only iron in the form of iron(III) the oxidation step may be omitted.

7.2.3 Acid soluble iron(II) and dissolved iron(II)

Transfer the test portion (7.1) to a 100 ml flask, add 2 ml of acetate buffer and mix thoroughly. The pH of the mixture should be between 3,5 and 5,5, preferably 4,5.

7.2.4 Acid soluble iron(III) and dissolved iron(III)

The concentration of acid soluble iron(III) or dissolved iron(III) is derived from the difference between the appropriate concentration of iron determined in 7.2.2 and the appropriate concentration of iron(II) determined in 7.2.3.

7.3 Blank test

Prepare a blank test solution using exactly the same procedure as for the test sample, but replacing the 50 ml of test portion with 50 ml of water.

7.4 Calibration

7.4.1 Preparation of reference solutions

Prepare a series of iron reference solutions to cover a range of concentrations appropriate to the expected iron concentration of the test sample by transferring appropriate accurately known volumes of the iron standard solution (4.8) to a series of one-mark volumetric flasks each of capacity 50 ml. Add 0,5 ml of dilute sulphuric acid (4.10) to each flask and make up to the mark with water.

Treat a series of iron reference solutions in a similar fashion to the test solutions, according to the appropriate procedure for each form of iron to be determined (see 7.2).

7.4.2 Formation of the absorbing compound

Add 2 ml of 1,10-phenanthroline solution (4.6) to each solution (7.4.1) and place them in the dark for 15 min.

7.4.3 Photometric measurements

Measure the absorbance of the solutions from 7.4.2 using the spectrophotometer or the absorptiometer (5.1) at 510 nm using water in the reference cell.

7.4.4 Plotting the calibration graphs

For each series of calibration solutions prepare a calibration graph by plotting the iron concentration of the test solution in milligrams per litre as abscissae against the corresponding measured absorbance as ordinate.

A separate calibration curve is required for each form of iron, for each photometric instrument and for each optical path length of cell.

7.4.5 Frequency of calibration

Check the calibration periodically and especially for each new batch of reagents.

7.5 Determination

7.5.1 Formation of the absorbing compound

To both the test solution (7.2) and the blank test solution (7.3), add 2 ml of 1,10-phenanthroline solution (4.6) and place in the dark for 15 min.

7.5.2 Photometric measurements

Measure the absorbance of the solutions from 7.5.1 using the spectrophotometer or the absorptiometer (5.1) at 510 nm using water in the reference cell.

NOTE — The molar absorption coefficient is 11 × 10^3 l/(mol·cm).

8 Expression of results

8.1 Calculation

The iron concentration, ϱ, expressed in milligrams per litre, of the sample is given by the equation

$$\varrho = f(A_1 - A_0)$$

where

f is the slope of the appropriate calibration graph (7.4.4);

A_1 is the absorbance of the test solution (7.5.2);

A_0 is the absorbance of the blank test solution (7.5.2).

NOTE — The volume of sulphuric acid added to the sample should be taken into consideration in the calculation.

8.2 Reporting the results

Report the results, by indicating the form of iron determined :

a) to the nearest 0,001 mg/l for iron concentrations from 0,010 up 0,100 mg/l;

b) to the nearest 0,01 mg/l for iron concentrations greater than 0,100 mg/l up to 10 mg/l;

c) to the nearest 0,1 mg/l for iron concentrations greater than 10 mg/l.

9 Precision

See the table.

Table — Statistical data on the repeatability of the method

Iron concentration mg/l	Laboratory	Path length[1] mm	Mean value of 30 results mg/l	Standard deviation mg/l
0,010	1	100	0,010	0,002
	2		0,010	0
	3	50	0,010	0,001
	4	10	0,010	0,011
	5	—	0,010	0,000
0,040	5	—	0,041	0,002
0,050	1	100	0,046	0,005
	2	—	0,048	0,004
	3	—	0,045	0,004 6
	4	10	0,048	0,011
0,100	1	50	0,104	0,015
	2	—	0,102	0,004
	3	—	0,096	0,006
	4	10	0,101	0,014
	5	—	0,099	0,006
0,500	1	50	0,48	0,025
	2	—	0,500	0,012
	3	—	0,494	0,005
	4	10	0,498	0,016
1,000	1	10	0,97	0,05
	2	—	1,003	0,008
	3	—	1,009	0,006
	4	10	1,004	0,019
	5	—	1,018	0,004
2,000	1	10	2,05	0,07
	3	—	2,016	0,008
	4	10	1,994	0,017
4,000	1	10	4,02	0,08
	3	—	3,989	0,013
	4	10	3,968	0,033
	5	—	4,003	0,019
5,000	1	10	5,01	0,07
	5	—	5,032	0,015

1) Where no path length is indicated, the path length was not specified by the laboratory.

10 Interferences

Determinations of iron concentrations using 1,10-phenanthroline are relatively free from interferences in comparison with other methods using other reagents. The following should be noted.

Copper, cobalt, chromium and zinc interfere if present in concentrations ten times that of the iron concentration. Nickel interferes if present in concentrations exceeding 2 mg/l. These interferences are avoided by adjusting the pH to between 3,5 and 5,5.

Bismuth and silver precipitate with 1,10-phenanthroline and the test solution must be completely free of their ions. Cadmium and mercury also form precipitates, but if present in low concentrations, appreciable interference is eliminated by adding excess 1,10-phenanthroline.

Cyanides interfere with the determination but are usually removed by acidification of the sample except in the case of some complex cyanides.

WARNING — Acidification of samples containing cyanide or sulphide ions must be carried out with care due to the formation of highly toxic vapours.

The acidification of the sample also converts pyrophosphates and polyphosphates to orthophosphates which do not interfere at PO_4^{3-} concentrations up to ten times that of the iron concentration. If higher concentrations are present, isolation of the iron as described in 7.2.1.2 is necessary.

Aluminium nitrate may be added to displace iron from complexes with certain other anions, such as phosphate, in which form the iron would be slow to react.

Interferences are generally removed by the procedure described in 7.2.1.2.

NOTE — It is not possible to include details for overcoming all the possible interferences that may be encountered in the application of this method, particularly to highly contamined water and industrial waste water. The method must be adapted according to the type of sample. In some cases, depending on the composition of the sample, an appropriate ashing treatment may be required, for example wet ashing with sulphuric and nitric acids or dry ashing, for example in a furnace at a temperature not exceeding 700 °C. In the presence of higher concentrations of chlorides losses of iron can occur.

11 Test report

The test report shall include the following information :

a) an identification of the sample;

b) the reference of the method used;

c) the results and the method of expression used;

d) the method of elimination of interferences;

e) any unusual features noted during the determination;

f) any operations not specified in this International Standard, or regarded as optional.